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SOLID-STATE ELECTROCHEMICAL PROCESSES IN DYE FILMS(U)
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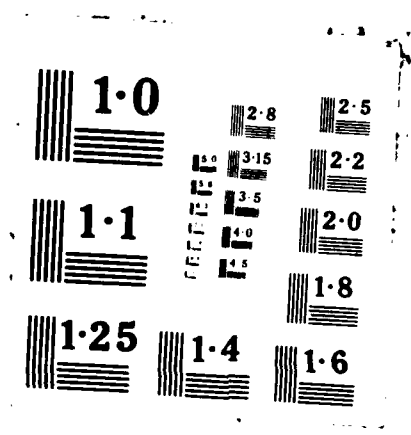
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Solid-State Electrochemical Processes in Dye Films

M. M. Nicholson

Science Center
Rockwell International Corporation
Anaheim, CA

November 1987

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Research on solid-state electrochemistry of lanthanide diphthalocyanine electrochromic films in the period 1977-1987 is summarized. Highlights include characterization of the ion-insertion processes with a novel solid-state moving-boundary technique, study of ambient-atmosphere effects on the anodic reactions, and investigation of solid polymer electrolytes for use in contact with diphthalocyanine electrode films. Future applications of these electrochromic systems in multicolor flat-panel information displays for military purposes are anticipated. (Key words)					
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SUMMARY

Multicolor electrochromism in lanthanide diphthalocyanine dye films was first reported by Soviet investigators.⁽¹⁰⁾ Starting with that information, we demonstrated, under a prior Navy contract, a strong potentiality for using the lutetium complex as the switchable material in a new type of flat-panel information display.⁽¹¹⁾ Virtually nothing was known at that time of the electrode processes responsible for these unusually fast, and cyclable, color changes. In 1977, we began a basic investigation of the electrochromism with coordinated sponsorship of the Office of Naval Research and the Air Force Office of Scientific Research. The Air Force program was concerned with reaction stoichiometries and kinetics at the interface between the dye films and liquid electrolytes. The ONR project, under the present contract, obtained information on processes occurring within the solid dye films and, at a later stage, sought to develop solid polymer electrolytes appropriate for interfacing with these materials in all-solid electrochromic cells.

The research began with the premise that the diphthalocyanine film must be conductive in all of its color states in order to support the high current densities and cycling characteristics observed. Since the initial green form was then assumed to be LnHPc_2 , it was conjectured that proton transport might play an important role in the electrochromism.

We devised a new solid-state moving-boundary technique for investigating processes in the solid dye as it underwent various color transitions.⁽¹⁾ This method provided, in effect, a slow-motion view of the electrode process. A red/green (or orange/green) reaction boundary was propagated in lutetium diphthalocyanine under constant anodic current. From the boundary velocity and the electric field in the oxidized phase, the carrier mobility and the number of electrons transferred per molecule of dye were determined. A related study by a radio tracer method showed that the anodic reaction occurred by the insertion of anions into the dye, rather than by loss of protons.⁽¹²⁾ With a chloride or sulfate electrolyte, the oxidation product was a solid anion conductor with a relatively high mobility of $4 \times 10^{-6} \text{ cm}^2/\text{V-sec}$ and an estimated bulk resistivity of 1,600 ohm-cm at room temperature.⁽¹⁾

A corresponding study of the cathodic electrochromism showed that cations were inserted during the faradaic reductions producing in blue or violet colors.⁽³⁾ Light blue products formed with neutral aqueous or organic solutions of alkali metals contacting the dye, while a dark violet product formed with acidic solutions. The dark violet phase had a hydrogen-ion mobility of $8 \times 10^{-7} \text{ cm}^2/\text{V-sec}$ and a bulk resistivity of approximately 1,800 ohm-cm.



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It was found that the gaseous environment could have a pronounced effect on the anodic reactions of lutetium diphthalocyanine.⁽²⁾ Water vapor was necessary to propagate the red/green boundary from aqueous electrolytes, and oxygen was essential in some instances with sulfate as the counter ion. The latter observation suggested that the diphthalocyanines may bind oxygen reversibly, thereby acquiring greater conductivity. Although the solid-state conduction was mostly ionic under sustained current flow, different behavior was observed immediately after reversal of the boundary-propagating current.⁽⁷⁾ The films then gave evidence of electronic conduction due to mixed oxidation states. The onset of such conduction may account for a complication encountered in switching electrochromic display films, where direct conversion from blue to green can be difficult.

The display application requires an electrolyte of relatively high conductivity. Solid ionic conductors are desired, and organic polymer electrolytes generally have physical properties compatible with the dye. However, it was considered important to augment the conductivity of candidate polymer systems by incorporating a solvent component, or plasticizer. Toward that objective, we investigated the influence of water on the conductivity of solid poly(ethylene oxide) (PEO)-lithium tetrafluoroborate films.⁽⁶⁾ Conductivities as high as $3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ were attained, but water in excess of the composition $\text{LiBF}_4 \cdot 3\text{H}_2\text{O}$ proved to be unstably absorbed and was lost spontaneously under constant water vapor pressure, with a drop in conductivity to $\sim 2 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$. The investigation of solid, or semisolid, polymer electrolytes was then extended to PEO-salt films plasticized with propylene glycol (PG)⁽⁸⁾ and solvent-swollen electrolyte films containing a polymer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS).⁽¹³⁾ The PEO- LiBF_4 -PG system also exhibited spontaneous loss of the plasticizer, but when HCl was present in addition to LiBF_4 , the loss was prevented, and a conductivity of at least $4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ was observed. When high-molecular-weight PEO-salt-PG materials were used with lutetium diphthalocyanine, the color changes were slow and nonuniform due to high interfacial resistance. However, semisolid AMPS type cells containing both water and PG, with some added HCl, showed rapid, uniform color changes and maintained interfacial contact at temperatures from -5 to 40°C. Further work on diphthalocyanine/solid electrolyte cells is desirable.

This research has led to related Rockwell projects with ONR on diphthalocyanine electrochromic display characteristics⁽¹⁴⁾ and to a transition of this technology into exploratory development under a larger current ONR program.⁽¹⁵⁾ It has also stimulated basic research and display development activities in several other countries. The science and technology of the lanthanide diphthalocyanine electrochromics are discussed in



three invited papers generated under this contract. (4,5,9) U.S. Navy applications ranging from cockpit displays to large-screen shipboard and command and control displays are possibilities for the future.



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